Organic light-emitting diodes based on a blend of poly[2-(2-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] and an electron transporting material

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Organic light-emitting devices (OLEDs) containing a blend of poly[2-(2-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH-PPV) and an electron transporting material, 2,7-bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazol-5-yl]-9,9-dihexylfluorene have been fabricated. The external quantum efficiencies of the OLEDs containing the electron transport compound were increased significantly over those obtained for devices based only on MEH-PPV. For example, the efficiency for a device incorporating 95% of electron transport compound was two orders of magnitude greater than that for a nonblended device. In all of our investigations, the electroluminescence (orange/yellow emission) originated exclusively from the MEH-PPV material, even for very high concentrations (>90%) of the electron transport component. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1776621]

Electroluminescence (EL) in organic materials is now the subject of intense worldwide research. For balanced charge injection, multilayer structures, for example incorporating both electron and hole transporting materials, are often fabricated.[1] As an alternative, single-layer organic light-emitting devices (OLEDs) using blends of conjugated polymers and carrier transport materials have been investigated.[2–4] Such devices have the advantage of easy manufacturing in terms of a single-spin-coating process. We have previously reported on single-layer OLEDs using blends of poly[2-(2-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH-PPV) with electron transport materials containing both oxadiazole and pyridine units.[5,6] In this work, an electron transport material, 2,7-bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazol-5-yl]-9,9-dihexylfluorene (DFD) has been blended with MEH-PPV. This compound contains both oxadiazole and fluorene units; oxadiazole to confer electron injection, and the fluorene unit to provide blue emission.

MEH-PPV was purchased from the Aldrich Chemical Co. while DFD was synthesized in Durham, U.K. Its chemical structure and synthesis are depicted in Scheme 1. Indium-tin-oxide (ITO)-coated glass from Merck with sheet resistance of 15 $\Omega\,\square^{-1}$ was used as the anode. ITO was patterned into 2 mm wide stripes by etching in $HCl:HNO_3:H_2O(1:0.08:1)$ solution at 50 °C. This substrate was cleaned by ultrasonification in acetone and isopropyl alcohol for 30 min each and dried with a nitrogen gun. The polymer and electron transport compound were dissolved in chloroform to provide the blend solution, which was spin coated onto the patterned substrate. In our experiments, the concentration of DFD was changed from 20% to 95% of the total weight. The thickness of the blend film was set to 120 nm by adjusting the concentration of the solution and the spin speed. Following the spin coating, 1.5 mm wide Al stripes (thickness 150 nm) were thermally evaporated perpendicular to the ITO stripes at a pressure of about 10^{-6} mbar. In some cases, poly(3,4-ethylenedioxythiophene) doped with polystyrene sulphonic acid [PEDOT:PSS, purchased from Bayer AG] was spin coated onto the substrate prior to the deposition of the polymer blend. These PEDOT layers (120 nm in thickness) were dried for 12 h. in 10^{-1} mbar vacuum at room temperature to remove residual solvent.

Electrical measurements were undertaken at room temperature with the OLED devices in a vacuum chamber (10^{-1} mbar) using instrumentation reported previously.[5,6] For absorption and photoluminescence (PL) measurements, the blend films were spin coated onto glass substrates. Absorption and PL spectra were measured with a Perkin Elmer Lambda 19 ultraviolet/visible/mean-IR spectrometer and a Fluoromax-3 spectrometer, respectively.

The current versus voltage ($I-V$) and light output versus voltage ($L-V$) characteristics of ITO/polymer blend/Al OLEDs are shown in Fig. 1 (positive bias applied to the ITO electrode). The $I-V$ and $L-V$ characteristics of an OLED based on a pure (nonblended) MEH-PPV layer are also shown for reference. It is evident that the current at a particular value of voltage decreased as the concentration of DFD was increased. Figure 1 also reveals that the light output from the blended OLEDs increased as the percentage of DFD in the blended layer increased from 20% to 70%, but decreased for higher concentrations of the electron transport compound. At 25 V, the light emission of the 70% DFD structure was eight times that of a pure MEH-PPV device at the same voltage. The brightness of this 70% device was 280 cd m^{-2} at a current density of 66 mA cm^{-2}. The increase of the light output over most of the composition range of the blended layer devices indicates an increase in the injection of electrons. The reason for the reduction in the light output for blends containing higher concentrations of DFD is not clear at present; the phenomenon is perhaps related to a decreasing hole current for blends consisting predominantly of the electron-transport compound.

The external quantum efficiencies of the blended layer OLEDs are shown in Fig. 2. These efficiencies increased with the concentration of DFD over the range of composition investigated. The device fabricated with a 95% blend was about 100 times more efficient than that of pure

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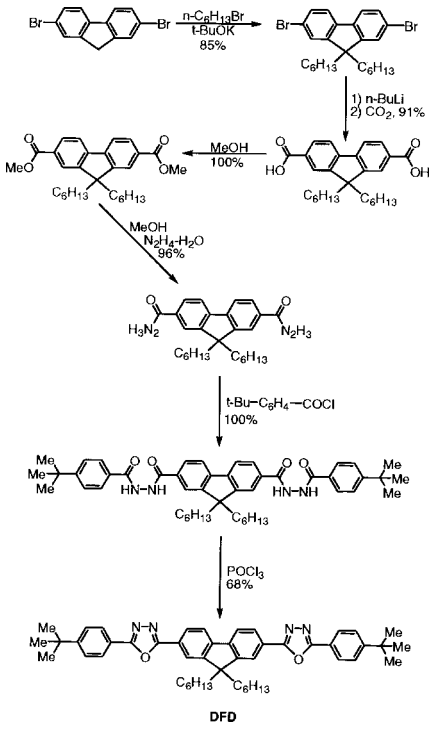

SCHEME 1. Chemical structure and synthetic scheme for DFD.

MEH-PPV (0.1% compared with 1×10^{-3}%).

Phase separation between constituent materials can be detrimental to OLED performance.[7] Structural defects such as clusters can act as quenching sites, increasing the nonradiative decay of singlet excitons. In our work, no sign of phase separation was evident using atomic force microscopy, although this is not a definitive method of determining the distribution of the two components. A "dilution" effect may be a contributory factor for the increase in our OLED efficiencies with increasing DFD concentration. As the polymer molecules become separated by the electron transporting molecules, concentration quenching—intermolecular nonradiative decay of singlet excitons—will be reduced resulting in an enhanced light output. Kang *et al.*[4] previously noted that the external quantum efficiency increased over seven times when MEH-PPV was blended with 90 wt% poly(methyl methacrylate), an electro-optically inert material. However, a much larger increase in efficiency (almost 500 times) was noted by mixing the MEH-PPV with another electroactive polymer.

Figure 3 shows the absorption spectra of DFD, MEH-PPV, and 90% DFD blend films and the PL spectra of DFD and 90% blend films. For the PL measurements, both the DFD and the 90% blend films were excited at 350 nm, the wavelength at which the absorption in the DFD is a maximum while the absorption in MEH-PPV is low. The absorption spectrum of the blend film has features attributable to both the DFD and MEH-PPV. The emission spectrum of the DFD overlaps to some extent with the absorption spectrum of the MEH-PPV, a necessary condition for efficient energy transfer between two materials.[8] The electron transporting material used in our study is itself a blue emitter (Fig. 3). However, no emission from the DFD was evident for the OLED containing the 90% blend. This again, suggests that the DFD and MEH-PPV materials are very well mixed in the blended film.

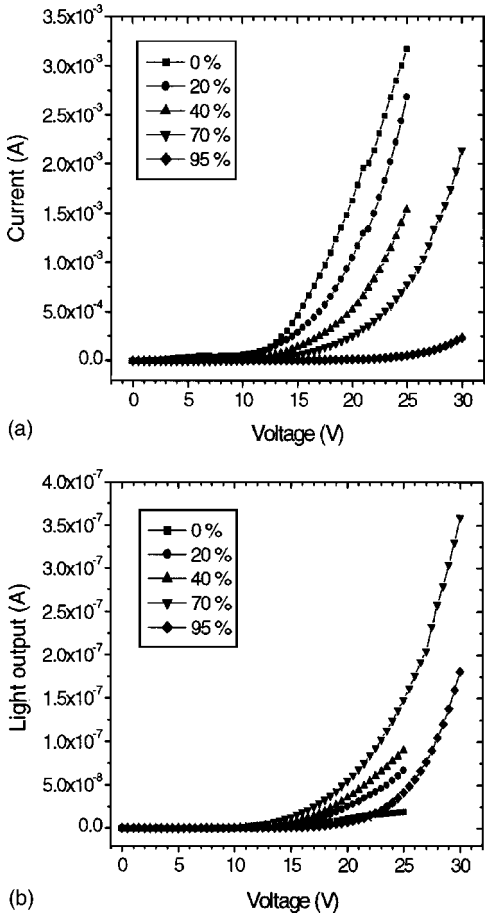

FIG. 1. (a) $I-V$ characteristics and (b) $L-V$ characteristics of MEH-PPV OLEDs fabricated using blends with various concentrations (by weight) of DFD. Positive bias applied to the ITO electrode.

The results of the PL experiments are reflected in the electroluminescent output of the OLEDs. Figure 4 shows the EL spectra of OLEDs using pure MEH-PPV, 50% and 90% DFD blend films. The EL spectra of OLEDs using blend films were very similar to the spectrum obtained from a pure MEH-PPV film. Emission from the DFD was not detected even at a high DFD concentration of 95%.

We have compared the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies for MEH-PPV and DFD using the semi-empirical PM3 method, where a ten-repeat-unit oligomer

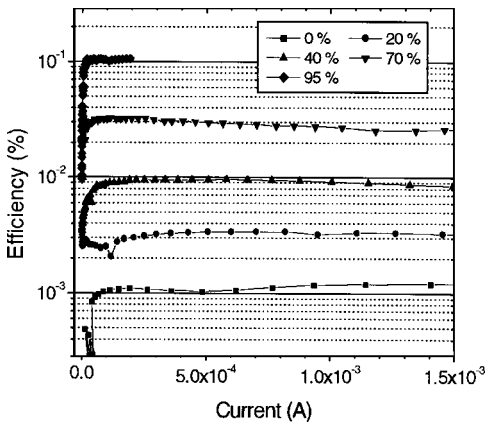

FIG. 2. External quantum efficiency versus current for OLEDs fabricated with MEH-PPV/DFD blended layers.

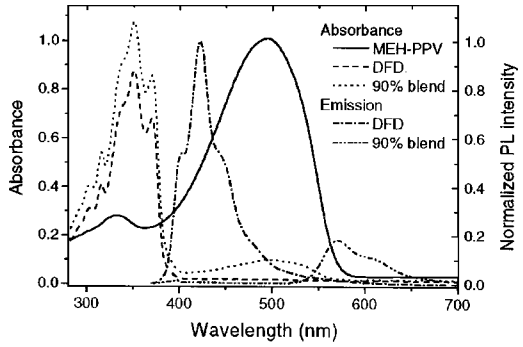

FIG. 3. Absorption spectra of DFD, MEH-PPV, and a 90:10 DFD:MEH-PPV blend; and PL spectra of DFD and a 90% blend excited at 350 nm. The PL spectra were normalized to the peak intensity of the DFD spectrum.

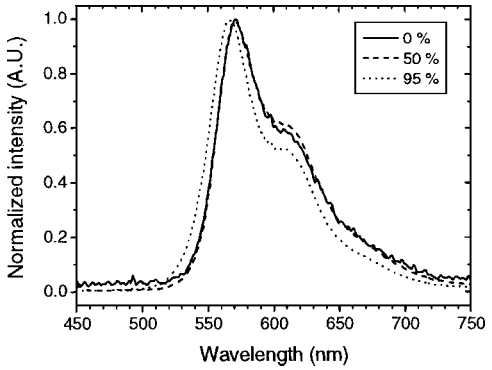

FIG. 4. Normalized electroluminescent spectra of OLEDs based on pure MEH-PPV; 50% DFD and 95% DFD.

of 2-methoxy-5-(2-methylpropyloxy)-1,4-phenylenevinylene was used instead of the MEH-PPV polymer.[9] The results indicate that the LUMO level of the DFD lies 0.1–0.2 eV below that of the MEH-PPV, while the difference between the HOMO levels of the two materials is three or four times this figure. Thus, holes are more likely to be transferred from the ITO electrode to the MEH-PPV but electrons will move from the Al cathode to the DFD. This provides an alternative and, perhaps more likely, explanation for our results than the energy transfer mechanism indicated above. For example, the excited MEH-PPV state can be formed by electron transfer from the DFD to the MEH-PPV. The relatively large difference in the HOMO levels of the MEH-PPV and DFD also explains the $I-V$ data shown in Fig. 1(a). As DFD concentration in the blended film increases, it will become more difficult to inject holes (the majority carriers) from the ITO into the blended film.

We have also undertaken preliminary work to improve further the characteristics of our blended layer devices (a) by incorporating a hole transport layer, PEDOT:PSS, between the ITO anode and the blended film and (b) by thermally annealing the devices. In this first case, the current and light output versus voltage behavior of OLEDs incorporating PEDOT as a function of DFD concentration was similar with those of OLEDs without the PEDOT layer (data not shown). However, the external quantum efficiency of OLEDs with the PEDOT layer were all increased by about a factor of 3, regardless of the concentration of DFD, giving a maximum external quantum efficiency for the OLED containing 95% DFD of 0.3%.

For our annealing experiments, we heat treated the OLEDs, following the Al deposition, at 160 °C for 1 h in a vacuum of about 10^{-4} mbar. In the case of the OLED fabricated with a pure MEH-PPV film, the external quantum efficiency increased by a factor of 20 after thermal annealing, consistent with our previous studies and those of other workers.[5,10,11] However, this efficiency improvement became less as the concentration of DFD was increased. For OLEDs containing more than 60% of the electron transport compound, the quantum efficiency of the devices was reduced after the heat treatment. These effects, which may be the result of some phase separation/crystallization of DFD in the blended layer OLEDs,[12,13] are currently the subject of further investigation.

In conclusion, single-layer OLEDs using blended films of MEH-PPV and an electron transport material, DFD, have been investigated. The external quantum efficiencies of the devices containing the electron transport compound increased significantly over those obtained for devices using pure MEH-PPV. The results argue well for the development of high efficiency OLEDs based on blended layers. However, further work is needed on the various processing steps in order to produce fully optimized devices.

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